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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Mechanism of Methylcyclohexane Ozonolysis

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Abstract—A mathematical model of selective oxidation of methylcyclohexane with ozone-oxygen mixtures was substantiated.

The methylcyclohexane molecule has three nonequivalent C-H bonds (at primary, tertiary, and five secondary carbon atoms at the α -, β -, and γ -positions relative to the methyl substituent). Therefore, selective oxidation of this molecule at a definite C-H bond can hardly be expected, the more so as thermal oxidation of methylcyclohexane with oxygen occurs at a noticeable rate only at elevated temperatures (above 120°C) and is low-selective [1].

The procedures for oxidation and analysis of reaction products were described in [2]. Ozonolysis of methylcyclohexane is active at 20°C (Fig. 1) and yields hydroperoxides, alcohols, ketones, acids, and esters.

Among methylcyclohexyl hydroperoxides formed by oxidation of methylcyclohexane, the major isomer (95–96%) is 1-methylcyclohexyl hydroperoxide. Among methylcyclohexanols, all possible isomers are detected (Table 1), with 1-methylcyclohexanol prevailing. The yield of the tertiary alcohol decreases with increasing conversion, temperature, and ozone concentration (Table 1, Fig. 1). Among isomeric methylcyclohexanones, 2-methylcyclohexanone prevails (Table 1). As the methylcyclohexane conversion increases, the yield of the alcohols and ketones decreases, with a simultaneous slight increase in the relative yield of hydroperoxides, acids, and esters (Fig. 2). The tertiary hydroperoxide at low temperatures (20°C) is consumed in the reaction with ozone slowly (rate constant $19 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$); therefore, its yield increases with conversion of methylcyclohexane. Ozonolysis of methylcyclohexane is highly selective with respect to the yield of 1-methylcyclohexanol at conversions of up to 12%. An increase in the yield of acids in the developed ozonolysis of methylcyclohexane is due to further oxidation of secondary and tertiary methylcyclohexanols and isomeric methylcyclohexanones.

Among carboxylic acids, ozonolysis of methylcyclohexane yields monocarboxylic, dicarboxylic, and keto acids. The ratio of the yield of monocarboxylic acids to the total yield of keto and dicarboxylic acids in the examined temperature range $(20-80^{\circ}C, [O_3] =$ 4 vol %) is 0.6-0.7 at the methylcyclohexane conversion of 12-82%. This ratio varies within a narrow range (0.4-0.7) [1] as the ozone concentration is varied within 2-4 vol %. The composition of the acids is given in Tables 2 and 3. Among monocarbox-



Fig. 1. Kinetic curves of accumulation of (a) hydroperoxides ROOH, (b) hydrogen peroxide H₂O₂, (c) ketones R=O, (d) alcohols ROH, (e) acids RCO₂H, and (f) esters RCO₂R' in oxidation of methylcyclohexane ($[O_3] = 4 \text{ vol } \%$). (t) Time; the same for Fig. 3. T, °C: (1) 20, (2) 40, and (3) 80; the same for Figs. 2 and 3.

TM OC	**	** 1		Alcohols, mo	Ketone, mol %		
····, ·C	a	τ,*** Π	1-MCHL	2-MCHL	3- + 4-MCHL	Ketone 2-MCHN 95 93 90 90 86 80	3- + 4-MCHN
20	12	2	93	5.5	1.5	95	5
	35	4	93	5.0	2.0	93	7
	57	6	90	8.0	2.0	90	10
40	20	2	85	12	3	90	10
	55	4	81	15	4	86	14
	77	6	75	16	9	80	20
80	35	2	80	15	5	85	15
	82	4	75	17	8	80	20
40***	26	6	95	4	Traces	96	4

Table 1. Composition of neutral products of methylcyclohexane ozonolysis ($[O_3] = 4 \text{ vol }\%$)*

* 1-, 2-, 3-, and 4-MCHL denote the respective isomers of methylcyclohexanol, and 2-, 3-, and 4-MCHN, the respective isomers of methylcyclohexanone.

** (a) Degree of conversion and (τ) ozonolysis time.

*** $[O_3] = 2 \text{ vol }\%.$

ylic acids, acetic acid prevails (70–87%). We also identified propionic, butyric, valeric, and capric acids. Among dicarboxylic and keto acids, we identified ε -ketoenanthic (16.2–35.1%), α - and β -methyladipic (40.7–53.2% in total), oxalic, succinic, methylsuccinic, α - and β -methylglutaric, and glutaric acids (Table 3). As the ozone concentration and temperature are increased, the yield of acetic and ε -ketoenanthic acids decreases. Keto acids are formed by ozonolysis of the tertiary hydroperoxide, 1- and 2-methylcyclohexanols, and 2-methylcyclohexanone [3–6].

Low-temperature ozonolysis of methylcyclohexane is a radical-chain reaction. Calculations show that, as in oxidation of cyclohexane, the chain-propagating



Fig. 2. Yield Φ_i of (a) hydroperoxides ROOH, (b) alcohols ROH, (c) ketones R=O, (d) acids RCO₂H, and (e) esters RCO₂R' as a function of methylcyclohexanol conversion at $[O_3] = 2$ vol %. (Σc_i) Sum of ozonolysis products.

species are alkoxy radicals rather than less active RO_2^{\bullet} radicals. Alkoxy radicals are apparently generated by recombination of tertiary peroxy radicals and by reaction of RO_2^{\bullet} radicals with ozone. The tertiary hydroperoxide is formed by cross recombination of RO_2^{\bullet} and HO_2^{\bullet} radicals and is mainly consumed with formation of 1-methylcyclohexanol.

At low (4–7%) methylcyclohexane conversions, ozonolysis occurs to 92–93% at the tertiary C–H bond. For example, at 20°C ($[O_3] = 0.5-2.5 \text{ vol }\%$), the total yield of 1-methylcyclohexanol and 1-methylcyclohexan hydroperoxide is 92–93%, that of other methylcyclohexanols and of methylcyclohexanones, 6–6.5%, and that of acids, 0.5–2%. The whole set of the data obtained allow us to propose the following mechanism of methylcyclohexane ozonolysis at low conversions:



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$$\bigcup_{i=1}^{CH_3} \underbrace{k_2 = 6.8 \times 10^{-3} \text{ s}^{-1}}_{O} + \text{HO}_2^{\circ}, \qquad (2)$$

$$\bigcup_{i=1}^{CH_3} + O_3 \xrightarrow{k_3 = 0.25 \, 1 \, \text{mol}^{-1} \, \text{s}^{-1}} \bigcup_{i=1}^{CH_3} + HO_3^{\bullet} + O_2^{\bullet}, \qquad (3)$$

$$HO_3^{\bullet} + O_3 \xrightarrow{\text{Slowly}} HO^{\bullet} + 2.5O_2, \tag{4}$$

$$HO_{2}^{\bullet} + HO_{3}^{\bullet} \xrightarrow{k_{5}^{\bullet} = 6.4 \times 10^{6} 1 \text{ mol}^{-1} \text{ s}^{-1}} H_{2}O_{2} + 1.5O_{2},$$
(5)

$$\bigcup^{CH_3}_{+ HO_2^{\bullet}} + HO_2^{\bullet} \xrightarrow{k_8 = 10^6} 1 \operatorname{mol}^{-1} \operatorname{s}^{-1} \qquad \bigoplus^{CH_3}_{- OOH} + O_2, \qquad (8)$$

$$\bigcup_{k_{9}=0}^{CH_{3}} + O_{3}^{k_{9}} \xrightarrow{k_{9}=1.1 \times 10^{3} \, 1 \, \text{mol}^{-1} \, \text{s}^{-1}} \bigoplus_{H_{3} C \, 0^{*}} + 2 \, O_{2}, \qquad (9)$$

$$\overset{\text{HOO}}{\longrightarrow} \overset{\text{CH}_3}{+} \overset{\bullet}{\longrightarrow} \overset{\text{O}}{\longrightarrow} \overset{\text{CH}_3}{\overset{\text{**= } 5 \times 10^4 \, 1 \, \text{mol}^{-1} \, \text{s}^{-1}} \overset{\bullet}{\longrightarrow} \overset{\bullet}{\longrightarrow} \overset{\text{OO}}{\overset{\text{CH}_3}{\longrightarrow}} \overset{\text{H}_3}{+} \overset{\text{C}}{\overset{\text{OH}}{\longrightarrow}}, \tag{10}$$

$$\overset{\text{H}_2}{\longrightarrow} \overset{\text{OOH}}{\longrightarrow} + O_3 \xrightarrow{k_{11} = 19 \times 10^{-3} \, 1 \, \text{mol}^{-1} \, \text{s}^{-1}} \overset{\text{H}_3}{\longrightarrow} \overset{\text{OO}}{\longrightarrow} + \text{HO}^{\bullet} + O_2, \qquad (11)$$

$$\begin{array}{c} & & \\ & &$$

HO' + HO'
$$\frac{k_{13}^{**} = 10^{10} \ 1 \ \text{mol}^{-1} \ \text{s}^{-1}}{\longrightarrow} \ \text{H}_2\text{O}_2,$$
 (13)

$$\begin{array}{c} & \overset{\text{CH}_3}{\longrightarrow} & + \overset{\text{CH}_3}{\longrightarrow} & \overset{k_{13}}{\longrightarrow} = 1.6 \times 10^6 \, 1 \, \text{mol}^{-1} \, \text{s}^{-1} & \overset{\text{CH}_3}{\longrightarrow} & + & \overset{\text{CH}_3}{\longrightarrow} & + & \text{O}_2, \end{array}$$

$$(14)$$

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	α, %	τ, h	Acid, mol %					
<i>I</i> , °C			C ₂	C ₃	C ₄	C ₅	C ₆	
20	12	2	69.8	13.4	5.0	5.0	6.8	
	35	4	71.0	12.5	4.7	5.0	6.5	
	57	6	74.0	10.0	5.0	5.3	6.1	
40	20	2	74.1	10.0	5.2	8.0	2.3	
	55	4	75.0	10.0	5.1	7.0	2.9	
	77	6	76.0	9.5	4.8	6.0	3.6	
80	35	2	76.0	9.5	2.9	7.0	4.5	
	82	4	80.0	8.3	3.5	5.0	3.0	
40	26	6	87.0	1.0	Traces	Traces	12.0	

Table 2. Content of monocarboxylic acids formed by ozonolysis of methylcyclohexane ($[O_3] = 4 \text{ vol } \%$)

Table 3. Content of keto and dicarboxylic acids formed by ozonolysis of methylcyclohexane ($[O_3] = 4$ vol %)

<i>T</i> , °C	α, %	τ, h	Acid, mol %						
			oxalic	methylsuccinic + succinic	glutaric and methylglutaric	ε-ketoenanthic	$(\alpha + \beta)$ -methyladipic		
20	12	2	15.0	7.5	11.6	20.6	45.4		
	35	4	13.0	7.0	12.0	18.8	49.2		
	57	6	12.5	6.9	12.4	16.2	52.0		
40	20	2	10.5	5.1	8.0	28.1	48.3		
	55	4	8.5	4.3	10.3	27.5	49.4		
	77	6	6.1	3.1	12.5	26.6	51.7		
80	35	2	4.0	2.7	10.8	32.3	50.1		
	82	4	2.7	2.1	11.5	30.5	53.2		
40	26	6	10.0	5.9	8.3	35.1	40.7		

where k^{**} are the estimated values of the constants, refined during further optimization.

The steady-state concentrations of the *i*th radical are determined from the condition $d[X_i]/d\tau = 0$. Taking into account the yields of products formed by the attack of ozone and radicals at the tertiary and secondary C-H bonds of the methylcyclohexane molecule, we can write



The rates of elementary reactions (1)–(14) of methylcyclohexane ozonolysis are expressed as follows: $R_1 = k_1[\text{RH}][O_3], R_2 = k_2[\text{ROOOH}], R_3 = k_3 \times$ [ROOOH][O₃], $R_4 = k_4$ [O₃][HO₃], $R_5 = k_5$ [HO₂] × [HO₃], $R_6 = k_6$ [O₂][R], $R_7 = k_7$ [RO₂]², $R_8 = k_8 \times$ [RO₂][HO₂], $R_9 = k_9$ [RO₂][O₃], $R_{10} = k_{10}$ [ROOH] × [RO⁻], $R_{11} = k_{11}$ [O₃][ROOH], $R_{12} = k_{12}$ [RH][RO⁻], $R_{13} = k_{13}$ [HO⁻]², and $R_{14} = k_{13}$ [RO²]². The initial reactant concentrations are [RH] = 7.8, $[O_3] = 1.3 \times 10^{-3}$, and $[O_2] = 5.6 \times 10^{-3}$ mol l⁻¹ s⁻¹. The concentrations of the radicals are found from the following relationships:

$$[\text{RO}_{2}^{'}] = [(2R_{2} + R_{4} + R_{11} + \beta R_{1})/(2k_{7}^{'})]^{1/2},$$

$$[\text{R}^{'}] = \frac{\beta R_{1} + R_{12}}{[\text{O}_{2}]k_{6}},$$

$$[^{'}\text{OH}] = [(\beta R_{1} + R_{4} + R_{11})/(2k_{13})]^{1/2},$$

$$[\text{HO}_{3}^{'}] = R_{3}/([\text{O}_{3}]k_{4} + k_{5}[\text{HO}_{2}^{'}]),$$

$$[\text{RO}^{'}] = (R_{2} + R_{3} + 2R_{7} + R_{9})/(k_{10}[\text{ROOH}] + k_{12}[\text{RH}]),$$

$$[HO_2] = (R_2 - R_3 + R_4)/([RO']k_8).$$

The constants k_5-k_7 , k_{10} , k_{12} , k_{13} , and k'_{13} were taken from [7–12], and the constants k_1 , k_9 , and k_{11} were measured by us in special experiments.

The rates of consumption of methylcyclohexane (RH) and accumulation of 1-methylcyclohexanol (ROH_t), 1-methylcyclohexyl hydroperoxide (ROOH), hydrogen peroxide, sum of secondary methylcyclohexanols (ROH_s), methylcyclohexanones (R=O), and hydrotrioxide (ROOOH) are described by the differential equations

 $d[RH]/d\tau = -R_1 - R_{12}, \quad d[ROH]_t/d\tau = R_{10} + R_{12} + \alpha R_1,$ $d[ROOH]/d\tau = R_8 - R_{10} + \alpha R_{11},$ $d[H_2O_2]/d\tau = R_5 + R_{13}, \quad d[ROH]_s/d\tau = \delta R_1 + k'_{13}[R'O_2^{\cdot}]^2,$ $d[R=O]/d\tau = k'_{13}[R'O_2^{\cdot}]^2, \quad d[ROOOH]/d\tau = \gamma R_1 - R_2 - R_3.$

Integration of this sytem of differential equations allows refinement of the constants $k_1-k_{13}^{**}$ and coefficients α , β , γ , and δ . The values of these parameters are given in the scheme of the mechanism of methylcyclohexane ozonolysis. The calculated data reasonably agree with the experiment (Figs. 1–3). The steadystate concentrations of the radicals are as follows: [RO₂] = (1.32–1.36) × 10⁻⁵, [RO⁻] = (3.62–3.68) × 10⁻¹⁰, ['OH] = (3.13–3.21) × 10⁻⁸, [HO₂] = (5.48– 5.72) × 10⁻⁷, and [HO] = (1.04–1.07) × 10⁻⁷ M (τ = 10–60 min).

According to the suggested mechanism, methylcyclohexane is consumed by the nonchain and chain pathways. Linear consumption (Fig. 3) is observed only at small conversions. In the developed process, the kinetic curves of methylcyclohexane (RH) consumption are nonlinear and are described by the following equation in the entire range of reactant concentrations up to deep conversions:

$$-d\left[\bigcirc CH_{3} \\ d\tau = k_{app}[RH] = k_{1app}[RH][O_{3}] \\ + k[([RH]_{2} - [RH])/[RH]].$$

Computer processing of the experimental data gave the following expressions: $k_{1app} = 1.25 \times 10^2 \times e^{-(25500 \pm 3500)RT}$ 1 mol⁻¹ s⁻¹ and $k = 3.5 \times 10^{-1} \times e^{-(25500 \pm 3500)RT}$ 1 mol⁻¹ s⁻¹.

The bimolecular rate constant of the reaction of 1-methylcyclohexyl hydroperoxide with ozone is low. However, in the developed reaction of methylcyclohexane ozonolysis, it is possible that the associate of 1-methylcyclohexyl hydroperoxide and 1-methylcy-clohexanol (their association was detected by ¹H



Fig. 3. Kinetic curves of consumption of methylcyclohexane RH ($[O_3] = 1.3 \times 10^{-3}$ M): (*I*) experiment and (*II*) calculation.



Fig. 4. Variation of the (1) specific activity A and of the rates ω of (2) formation and (3) consumption of 1-methyl-cyclohexyl hydroperoxide in the course of methylcyclohexane ozonolysis (20°C, $[O_3] = 4$ vol %).

NMR [13]) reacts with ozone at the same rate as does nonassociated 1-methylcyclohexyl hydroperoxide. To reveal the role of this reaction in the overall ozonolysis of methylcyclohexane, we added at the stage of the developed reaction (20°C, $[O_3] = 4 \text{ vol } \%$, 30 min after the start of the experiment)¹⁴C-labeled 1-methylcyclohexyl hydroperoxide. The specific activity of the added hydroperoxide decreases (Fig. 4) owing to both its consumption and dilution with the forming nonradioactive 1-methylcyclohexyl hydroperoxide. The labeled compound transforms into the following ¹⁴C-labeled products: 1-methylcyclohexanol, ε-ketoenanthic acid, and acetic acid. From variation of the specific activity of the hydroperoxide in the course of the experiment, we calculated the rates of its formation. Taking into account the experimental rates of 1-methylcyclohexyl hydroperoxide accumulation, we calculated the rates of its consumption (Fig. 4).

Among the products of 1-methylcyclohexyl hydroperoxide transformations, 1-methylcyclohexanol comprises only 6-7%. An increase in the rate of formation of the tertiary hydroperoxide with the conversion of

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the hydrocarbon is apparently due to increase in the rate of HO₂ generation. Unstable methylcyclohexyl hydrotrioxide may be a source of HO₂. A decrease in the yield of hydrogen peroxide (Fig. 1), seemingly contradicting this assumption, may be due to catalysis of its decomposition with acids.

CONCLUSION

In contrast to nonselective high-temperature noncatalytic oxidation of saturated hydrocarbons containing primary, secondary, and tertiary C–H bonds, their low-temperature ozonolysis at small conversions, as demonstrated by the example of methylcyclohexane, occurs selectively at the tertiary C–H bond and yields the corresponding alcohols. The tertiary alcohols are formed by recombination of the R[•] and OH[•] radicals generated by primary initiation, by radical-chain transformations of tertiary hydroperoxides, and by attack of the starting substrate by RO[•] radicals.

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